

Controls over N_2O , NO_x and CO_2 fluxes in a calcareous mountain forest soil

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Abstract. We measured nitrogen oxides (N_2O and NO_x), dinitrogen (N_2) and carbon dioxide (CO_2) emissions from a spruce-fir-beech forest soil in the North Tyrolean limestone Alps in Austria. The site received $10.6\text{--}11.9\text{ kg N ha}^{-1}\text{ y}^{-1}$ nitrogen as bulk deposition. Fluxes of nitric oxide (NO) were measured by an automatic dynamic chamber system on an hourly basis over a two year period. Daily N_2O emissions were obtained by a semi-automatic gas measuring system. In order to cover spatial variability biweekly manual measurements of N_2O and CO_2 emissions were carried out in addition. For acquiring information on the effects of soil and meteorological conditions and of N-deposition on N-emissions we chose the auto-regression procedure (time-series analysis) as our means of investigation. Hence, we could exclude the data's autocorrelation in the course of the time. We found that soil temperature, soil moisture and bulk N-deposition followed by air temperature and precipitation were the most powerful influencing parameters effecting N-emissions. With these variables, up to 89% of observed temporal variations of N-emissions could be explained. During the two-year investigation period between 2.5 and 3.5% of deposited N was reemitted in form of N_2O whereas only 0.2% were emitted as NO . At our mountain forest site the main end-product of microbial activity processes was N_2 and trace gases (N_2O and NO) were only of minor importance.

1 Introduction

Nitrous oxide (N_2O) is a stable greenhouse gas in the troposphere and is involved directly in global warming. In the stratosphere it is responsible for the catalytic decomposition of ozone (Crutzen, 1979). The increase in the atmosphere is reported at present to be about 0.25% per year (IPCC, 2001). As the potential of global warming of N_2O is 300 times higher than that of carbon dioxide (CO_2) a further increase of atmospheric N_2O concentration might affect global climate even more in the future.

In contrast, nitric oxide (NO) is indirectly involved in global warming and contributes to the net production of radiative tropospheric ozone and photochemical air pollution (Crutzen, 1995; Firestone and Davidson, 1989; Williams et al., 1992).

The production of N_2O , NO , and N_2 in soils is mainly the result of nitrifying and denitrifying bacteria (e.g. Davidson et al., 2000; Conrad, 1996; Lovett et al., 2002). These microbial activity processes and thus the production rates of NO , N_2O and N_2 , are influenced by various factors. These drivers are temperature, precipitation, total N, availability of O_2 , mineralization rate, respiration, texture and structure, available nitrogen, pH and tree species composition (Davidson et al., 2000; Ludwig et al., 2001; Simek and Cooper, 2002). As forest soils are generally not treated with N fertilizers, N deposition from the atmosphere which are mainly due to NH_3 release from agricultural practices and NO_x release from combustion processes provides a considerable increase in mineral N input to forest soils. Atmospheric N-deposition is estimated to be at least $5\text{ kg N ha}^{-1}\text{ y}^{-1}$ in most regions of Europe, but can reach up to $50\text{ kg N ha}^{-1}\text{ y}^{-1}$ in Central and Northern Europe (NADP, 2002). Nitrogen surplus in forest

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Table 1. Site and soil characteristics of the investigation site Achenkirch.

Location	47°34'50'' N 11°38'21'' E
Vegetation	Aposerido-Fagetum caricetosum albae – Carici albae-Fagetum ^{a)}
Stand age [yr]	127
Exposition, elevation [m]	N, 895 m a.s.l.
Tree height [m]	19.1
Basal area [m ² ha ⁻¹]	40
Soil type	Rendzic Leptosols/Chromic Cambisol
Soil texture	loam
Soil acidity 0–7 cm (pH CaCl ₂)	5.8–7.1
C:N	16–18
Mean precipitation [mm]	1733 ^{b)}
Mean air temp [°C]	6.52 ^{b)}
Soil density [g cm ⁻³]	0.6
N _{tot} [mg g ⁻¹] 0–15 cm	9 ^{c)}
C _{org} [mg g ⁻¹] 0–15 cm	150 ^{c)}

^{a)} Englisch and Starlinger 1995,

^{b)} Mean of years 1998–2003,

^{c)} Mutsch 2001.

soil can be stored as soil N, taken up by microbes and plants or leached into groundwater. It can alter the rates of microbial N- and C- turnover in soil or it can be nitrified and denitrified to gaseous products of NO, N₂O and N₂ (Skiba et al., 2004). Increased N-deposition can lead to changes in soil chemistry, forest composition and forest productivity.

A deposition of 12 kg ha⁻¹ y⁻¹ of nitrogen at the study site Achenkirch (AK) is moderate but exceeds Critical Loads according to the WHO-Guideline (WHO, 1995) for sensitive coniferous forest ecosystems (Smidt et al., 1996). In other alpine areas an input of up to 30 kg ha⁻¹ y⁻¹ was found (Herman et al., 2002) and increased flux rates of atmospheric greenhouse gas emissions (NO, N₂O, CO₂, CH₄) might be expected. However, only limited information is available about effects of atmospheric N deposition on the biosphere-atmosphere exchange of N trace gases in alpine forest ecosystems. For the estimation of global budgets such measurements are needed. During a two-year sampling period of CO₂, N₂O and NO_x emissions, measurements were carried out in order to (1) investigate the trace gas exchange between a typical spruce-beech-fir forest soil in the limestone Alps and the atmosphere. Measurements were conducted in high temporal and spatial resolution to (2) get better estimates of annual emissions, (3) study the relationships between N-trace gas emissions and meteorological factors and soil parameters, (4) investigate if N-deposition affects N-emissions in these forest ecosystems and (5) find an appropriate statistical procedure to describe the relationships between N-emissions and their ecological drivers.

2 Material and methods

2.1 Investigation site and soil

The 127 year old forest is located in the Achenal of the North Tyrolean limestone Alps, and was described by Englisch and Starlinger (1995) as a warm, central-montane spruce-fir-beech forest. The Mühleggerköpfl is a completely isolated hill, formed from dolomite, at a height of 895 m above sea level. The soils are mainly Rendzic Leptosols and Chromic Cambisol and are characterized by a high clay content and a low percentage of coarse material in the upper 10 cm. The soil properties are characterized by a high spatial heterogeneity. The depth of the A-horizon varies from 10–35 cm. For this horizon the organic matter content is very high (>10%). Mean pH is 6.42. (For site description see Table 1). A detailed description of the site is given in Herman et al. (2002).

2.2 N₂O and CO₂ flux measurements

Gas measurements were carried out as described in Kitzler et al. (2006). Gas samples of four manually operated chambers (area: 1 m², volume: 80 l) were taken biweekly from May 2002 until July 2004. Duplicate air samples from the chambers were taken after 0, 1 and 2 h and injected into gas tight head-space vials (20 ml). Linearity of emission was always tested. We never observed a flattening of the N₂O increase in our chambers, which would indicate an approach of the compensation point for N₂O. Additional measurements every 15 minutes showed that the increase in N₂O concentrations remained linear for up to 4 hours (Zechmeister-Boltenstern et al., 2002).

Daily (1/day) samples were taken by the automatic gas sampling system (AGPS – patent DE 198 52 859) and vials were collected every two weeks. The system is described in detail by Kitzler et al. (2006). Gas samples were stored at 4°C until analysis.

Gas samples were automatically drawn at 6 a.m. The time was chosen based on observations that emission rates were higher in the morning. Seven diurnal measurements at different times of the year showed, that between 4 and 10 a.m. and again in the afternoon slightly higher emissions were measured, but no regular daily trend could be observed. Furthermore, a high variability was detected on successive days. At each manual sampling time we made a measurement with the AGPS to ensure, that with our timing of the AGPS system reliable estimates can be made. The N₂O concentrations of manually and automatically drawn samples were of similar magnitude and well within the range of spatial variability. In order to avoid freezing of the covering case on the sealing plate, the thermostat was set to 1°C and there were no measurements conducted below this temperature. During winter no automatic measurements were carried out, but manual measurements were carried out as long as the site was accessible. Emissions of N₂O (μg N m⁻² h⁻¹)

and CO₂ (mg C m⁻² h⁻¹) were determined by the linear increase of the mixing ratio within the incubation period. Nitrous oxide and CO₂ fluxes were calculated as described in IAEA (1992). Annual rates were calculated by weighting hourly emission rates with the exact period between sampling times. Emissions from the manual system are presented for the first investigation year (May 2002–April 2003) and for the second investigation year (May 2003–April 2004). With the AGPS (N₂O-N AGPS) no measurements were made during winter, calculated emissions are presented for June–November 2002 and May–November 2003. A gas chromatograph (HP 5890 Series II) with a ⁶³Ni-electron-capture detector (ECD), connected to an automatic sample-injection system (DANI HSS 86.50, HEADSPACE-SAMPLER) was used for N₂O analysis. The oven, injector and detector temperatures were set at 120°C, 120°C and 330°C, respectively. A standard of 5 μl l⁻¹ N₂O (Linde Gas) was used and dilution series (5; 2.5; 1.25; 0.625; 0.25 vppm) were made regularly. Standards were placed after each batch of 12 samples. Dinitrogen in ECD-quality with a flow rate of 30 ml min⁻¹ served as carrier-gas. We quantified a minimum detectable N₂O flux of 0.04 μg N m⁻² h⁻¹ and the relative error falls below <17% with a median of 5%. Carbon dioxide was analysed by using a gas chromatograph (Hewlett-Packard 5890 II series) equipped with a thermal conductivity detector (TCD). Helium was used as carrier-gas (flow rate 10 ml min⁻¹); the CO₂ standard contained 10 ml l⁻¹ CO₂ (Linde Gas) and dilution series (10 000; 5000; 2500; 1250; 500 vppm) were made regularly. Standards were placed after each batch of 12 samples. The detection limit for CO₂ flux was 0.001 mg C m⁻² h⁻¹.

2.3 NO_x flux measurements

Continuous measurements of NO_x were completed by a fully automated system (Holtermann, 1996), at an hourly frequency. NO_x was measured with a HORIBA APNA-360 chemoluminescence NO_x analyzer (detection limit: 1 ppbv NO or 0.6 μg NO-N m⁻² h⁻¹, 1 ppbv NO₂; flow rate: 1 l min⁻¹). The reading for NO_x of the HORIBA analyzer refers to NO, NO₂ and other nitrogen compounds (PAN, NH₃, HONO, HNO₃, aerosol ammonium, nitrate and nitrite). We therefore use the terms NO and (NO_x-NO) further on. The median error was <15% and <35% for NO and NO_x-NO, respectively. Calibration was conducted monthly by using a HORIBA calibration unit (Transferstandard, ASGU-360, 0–600 ppb). The quality of calibration near the detection limit was <1%. To avoid reactions of NO and O₃ in the chambers, a filter cylinder, filled with Purafil and activated charcoal, was applied in front of the chambers in year 1 (May 2002–April 2003) as no ozone analyzer was available in this year. In the second year (May 2003–April 2004) we used an ozone analyzer (HORIBA APOA-360) for measuring O₃ concentrations within the chambers. Thus, the chemical reaction between NO and O₃ could be considered. No filter

was applied in this year.

Air samples were taken from 5 stainless steel chambers (ø=20 cm; Vol.=3.27 l), plus one reference chamber where the opening to the soil was sealed with a Plexiglas pane. Each chamber was closed (Plexiglas lid) for 5 min within which steady state was reached. For the calculation of the fluxes of the first year we followed the protocol of Schindlbacher et al. (2004), and for the second year the protocol of Butterbach-Bahl et al. (1997). For corrections in the tubings see also Beier and Schneewind (1991) and for corrections in the dynamic chambers Remde et al. (1993) and Ludwig (1994). For further details on analysis of gas samples and calculation of fluxes compare Kitzler et al. (2006). Ozone can strongly absorb to the chamber wall and to tubes and does effect the gas phase correction of NO and NO₂ fluxes. An error analysis indicated that O₃ absorption at the chamber walls was negligible and no correction of fluxes was deemed necessary. Even a 30% decrease of O₃ concentration would have changed the NO flux by less than 0.2 μg N m⁻² h⁻¹ which is in our case smaller than the detection limit. The measured pressure deficit (Pressure sensor: PCLA 12X5D Sensor Technics) in our chambers is < than 0.6 Pa and irrelevant for N-fluxes. The residual aerodynamic resistance was determined as suggested by Ludwig (1994) and was 61 s m⁻¹. This value is in accordance to published values (55 and 60 s m⁻¹) by Meixner et al. (1997) and Gut et al. (2002).

2.4 Soil samples

Soil samples were taken approximately every two months. Extractable nitrogen was determined from litter layer (frame: 30×30 cm) and mineral soil (upper 7 cm), and analysed according to Kandeler (1995). Soil moisture was determined gravimetrically. The pH was measured in soil suspensions in 0.01 M CaCl₂ solution using a glass electrode. Additionally to these analysis, an acetylene (C₂H₂) inhibition experiment was carried out twice (May 2003 and August 2003). Acetylene inhibits the reduction of N₂O to N₂ and is used to quantify the total N-emission (N₂O+N₂) that is produced via denitrification (Klemmedtsson et al., 1990). Per sampling time 16 soil cores from the upper 5 cm mineral soil were incubated in airtight incubation cylinders (volume: 500 ml) and sealed with silicon grease. The headspace air of the cylinders was sampled (30 ml) at the beginning of the incubation period and after 4 h at a temperature of 25°C; thus allowing the determination of N₂O production. Afterwards, acetylene was introduced into the head-space, exposing the soil core to 10 kPa acetylene. Gas sampling procedure and incubation of the acetylene treated samples was the same as for non treated samples. Gas samples were analyzed for N₂O as described in Sect. 2.2. The difference between acetylene treated and untreated N₂O production was calculated to be the N₂ production at the time of soil sampling (May 2003 and August 2003). Water filled pore space of soil samples was 43% and 46%.

Table 2. Mean soil nitrogen [$\mu\text{g N g}^{-1}$ dw] and pH (CaCl₂) in the litter layer and in the upper 7 cm mineral soil in year 1 (May 2002–April 2003) and year 2 (May 2003–April 2004) at Achenkirch.

	year 1		year 2	
Litter layer				
NH ₄ ⁺ -N	65.8	(8.5)	43.1	(4.0)
NO ₃ ⁻ -N	31.4	(4.4)	18.3	(2.2)
pH (CaCl ₂)	6.1	(0.1)	5.8	(0.1)
Mineral soil				
NH ₄ ⁺ -N	21.0	(3.0)	8.8	(1.2)
NO ₃ ⁻ -N	1.5	(0.3)	2.1	(0.3)
pH (CaCl ₂)	6.5	(0.1)	6.3	(0.1)

Note: Soil data are means with standard error in parenthesis.

2.5 Meteorological data

Soil temperature (in °C, Vitel-thermistors) and soil moisture data (in %, Vitel – Theta probes) were quantified at a soil depth of 5, 15, 25 and 50 cm and stored in a data logger. Air temperature (°C) was measured with a LTK-592 C sensor (Inc. Sommer) at 2 m above ground in a standard weather station. Measuring interval was 4 h. As far as the manual gas sampling time was concerned, soil temperatures at a soil depth of 3 and 10 cm were additionally measured around the chambers. Daily precipitation was recorded by an ombrometer at the nearby meteorological station – Pumpwerk Achenkirch. The biweekly input below the crown was calculated from the crown throughfall collectors.

2.6 Deposition measurements

Dry N-deposition comprises NH₃ and NO₂, NO (if soil compensation mixing ratio is exceeded), HONO, HNO₃, PAN, aerosol ammonium, nitrate and nitrite. In this study, concentrations of NH₃ were captured by three passive diffusion tubes (Tang et al., 2001) and were analysed at CEH Edinburgh.

In this study the samplers were placed in the canopy at the investigation site at a height of 1.5 m and were changed monthly. Dry deposition velocities were assumed to be 3 mm s⁻¹ for NH₃ (Duyzer, personal communication). Bulk deposition was collected biweekly using 15 crown throughfall collectors. Bulk deposition was analysed for NH₄⁺-N and NO₃⁻-N (Dionex DX100 and Dionex 120). Concentration of NH₃ was measured in the first investigation year (May 2002–April 2003), whereas bulk deposition was measured in the first and the second investigation year (May 2003–April 2004).

Table 3. Sum of bulk and sum of NH₃ deposition [$\text{kg N ha}^{-1} \text{y}^{-1}$] and precipitation via throughfall in year 1 (May 2002–April 2003) and year 2 (May 2003–April 2004) at the study site Achenkirch.

	year 1	year 2
Precipitation [mm]	1416	1067
N-input by bulk deposition/throughfall [$\text{kg N ha}^{-1} \text{y}^{-1}$]		
NH ₄ ⁺ -N	3.5	4.6
NO ₃ ⁻ -N	7.1	7.3
Sum of bulk deposition	10.6	11.9
N-input by dry deposition [$\text{kg N ha}^{-1} \text{y}^{-1}$]		
NH ₃ -N	0.56	n.d.

n.d. = not determined.

2.7 Statistical analysis

Data were checked for normal distribution. The t-test or the nonparametric Wilcoxon-test was used for determining differences in soil emissions, soil chemical and N-deposition data between the investigation years. Pearson or Spearman rank correlation was used for determining relations between daily or biweekly emission data and soil, meteorological or deposition data. A moving average of 2 was applied for deposition data.

As variables are autocorrelated in the course of time (Durbin-Watson statistic), the autoregression procedure – GARCH (p , q) model (generalized autoregressive conditional heteroscedasticity model) – was used to detect influences of soil data, meteorological- or deposition data on N-emissions. Specifications of the GARCH model are described in detail in Kitzler et al. (2006). Variables that emerged to correlate best with N₂O and NO emissions and variables, whose effects on emissions were lagged, were incorporated in the models. Statistical analysis was either completed using SAS Enterpriseguide Version 2 or SAS Version 8. All differences reported were significant at $p < 0.05$ unless otherwise stated.

3 Results

3.1 Soil nitrogen and pH

Concentrations of extractable N in the litter layer were at their highest after litterfall in autumn and reached a maximum of 138 $\mu\text{g NH}_4^+\text{-N g}^{-1}$ dw (dry weight) and 80 $\mu\text{g NO}_3^-\text{-N g}^{-1}$ dw in September 2002 (Fig. 1). Mean NH₄⁺-N and NO₃⁻-N concentrations of the first year were considerably higher than the concentrations measured in the second year (Table 2). A similar seasonality was also observed with regard to N concentrations in the mineral soil. Here, up to 7.9 $\mu\text{g NO}_3^-\text{-N g}^{-1}$ dw (year 1) and up to 50 $\mu\text{g NH}_4^+\text{-N g}^{-1}$ dw (year 2) were reached in autumn. In the second

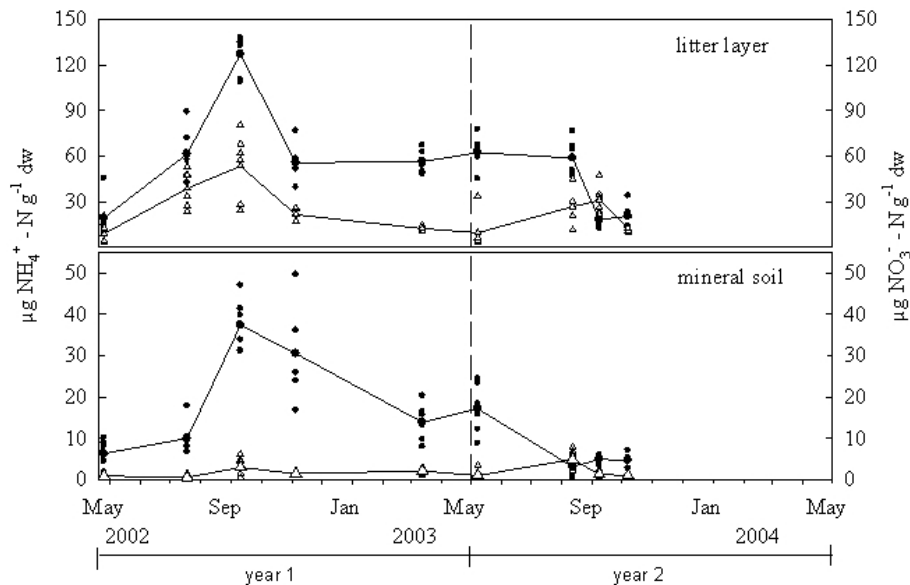


Fig. 1. Extractable NH₄⁺-N (circles) and NO₃⁻-N (triangles) in the litter layer and in the mineral soil at Achenkirch in the first investigation year (May 2002–April 2003) and the second investigation year (May 2003–April 2004). The straight line indicates the mean. Pooled samples (n=4) were taken from around the individual chambers.

year considerably lower NH₄⁺-N concentrations were detected, particularly in autumn. Mean soil pH was 6.4 with a maximum of 7.0 and a minimum of 5.4. PH of the litter layer was generally lower (mean=5.9) and ranged from 5.1–7.1.

3.2 Nitrogen input

In the two years of investigation, the N-input via through-fall amounted to 10.6 kg and 11.9 kg N ha⁻¹ y⁻¹ (Table 3). Ratio of deposited NO₃⁻-N:NH₄⁺-N is 1.7:1. In general, N from throughfall had its maximum in spring/early summer. In the second year, however, the highest bulk N-deposition was detected in autumn (Fig. 2). No relationship was found between precipitation rates and N-input. Concentrations of NH₃ were as high as 7.7 µg NH₃ m⁻³ in the first year (May 2002–April 2003), respectively. The forest floor received 21.6 kg N ha⁻¹ y⁻¹ (1999) through litterfall (Herman et al., 2002).

3.3 Gas fluxes

3.3.1 CO₂ fluxes

Maximum CO₂ emissions were recorded in summer, following a seasonal course of air and soil temperature (Fig. 3a). In the first investigation year the summer peak was not as pronounced and summer emissions were significantly (p<0.01) smaller than in the following year. In late autumn emissions decreased steadily and reached a minimum in winter (0.0–0.2 mg CO₂-C m⁻² h⁻¹).

Table 4. Mean CO₂-C (mg C m⁻² h⁻¹), N₂O-N and NO-N emissions (µg N m⁻² h⁻¹), minimum and maximum values and number of observations at Achenkirch. (year 1: May 2002–April 2003 and year 2: May 2003–April 2004). Mean NO-N emissions are calculated for a) June–November 2002 and b) May–November 2003.

		CO ₂ -C	N ₂ O-N	NO-N
		[mg C m ⁻² h ⁻¹]	[µg N m ⁻² h ⁻¹]	
year 1	mean	11.6	4.5	0.7 ^a
	min-max	(0–56.4)	(–3.5–34.0)	(0.4–2.5)
	N	95	242	105
year 2	mean	19.7	4.4	0.5 ^b
	min-max	(0.4–83.0)	(–2.9–40.6)	(–0.1–7.6)
	N	96	288	145

NO-N emissions are calculated for a) July–October 2002 and b) May–November 2003.

Mean CO₂ emission were 11.6±1.1 mg CO₂-C m⁻² h⁻¹ (year 1) and 19.7±2.0 mg CO₂-C m⁻² h⁻¹ (year 2) showing a significant difference between the two years (Table 4). At our site the cumulative soil respiration rate was 1.3±0.3 t C ha⁻¹ y⁻¹ (Table 5) with a 60% higher annual CO₂ production rate in year 2.

The most influencing parameters controlling CO₂ emissions were soil temperature at a soil depth of 3–25 cm (r²=0.86) and air temperature (r²=0.70).

Table 5. Measured and predicted CO₂-C (\pm S.E) [kg C ha⁻¹ y⁻¹], N₂O-N emissions (\pm S.E) [kg N ha⁻¹ y⁻¹] from the manual chambers for the two investigation years at the site Achenkirch (year 1: May 2002–April 2003 and year 2: May 2003–April 2004); N₂O-N (AGPS) and NO-N emissions [kg N ha⁻¹ y⁻¹] are calculated for a) June–November 2002 and b) May–November 2003.

	CO ₂ -C	N ₂ O-N (manual)		N ₂ O-N (AGPS)		NO-N	
	kg C ha ⁻¹ y ⁻¹	kg N ha ⁻¹ y ⁻¹					
	measured	measured	predicted ^{1,2}	measured	predicted ³	measured	predicted ⁴
year 1	1020±241	0.30±0.11	0.36±0.04 0.33±0.03	0.22±0.02 ^{a)}	0.28±0.01	0.03±0.002 ^{a))}	0.03±0.001
year 2	1636±283	0.41±0.09	0.26±0.04 0.38±0.04	0.19±0.02 ^{b)}	0.23±0.01	0.03±0.004 ^{b)}	0.03±0.004

^{1–4} Model 1–Model 4.

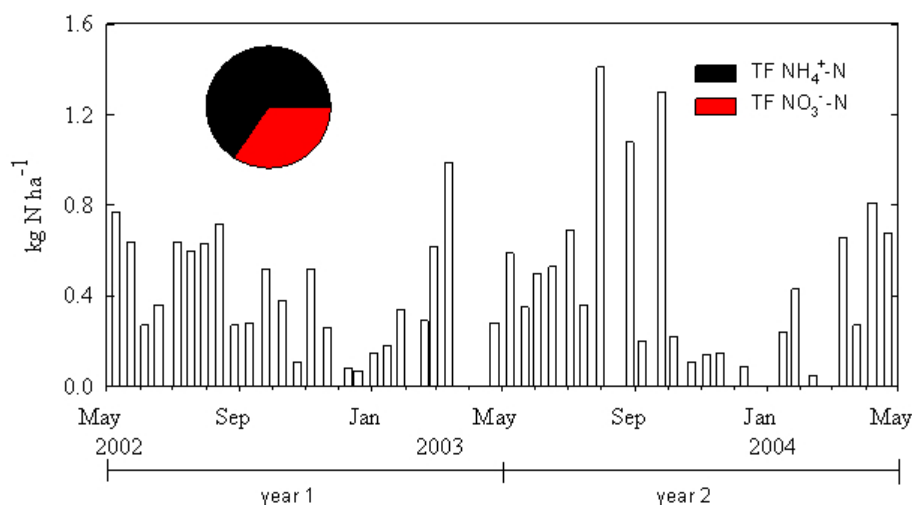


Fig. 2. Bar chart: Biweekly N-input (kg N ha⁻¹) at Achenkirch measured in the two investigation years. Pie chart: Portion of throughfall (TF NH₄⁺-N, TF NO₃⁻-N) on annual N-input (kg N ha⁻¹) in the first investigation year (May 2002–April 2003).

3.3.2 N₂O fluxes

Nitrous oxide emissions were mostly dependent on air and soil temperature, as well as on soil moisture. Figure 3b shows spatial and temporal variability during the investigation years. Spatial variation between the chambers was high (mean CV: 50%) and reached a maximum in winter (CV: 350%).

Mean N₂O emissions averaged $4.4 \pm 0.3 \mu\text{g N m}^{-2} \text{ h}^{-1}$ (Table 4). In the course of the year largest N₂O emissions were observed in summer 2003 ($40.6 \mu\text{g N m}^{-2} \text{ h}^{-1}$). Although we missed the summer peak with the manual chamber system in the first year, we were able to observe large N₂O emissions by the AGPS (Fig. 3b). During winter, when the site was covered with snow, a significant uptake of atmospheric N₂O (range: -0.3 to $-3.5 \mu\text{g N m}^{-2} \text{ h}^{-1}$) could be observed. Significant correlations could be found between C- and N-emissions, and soil, meteorological and N-input

data (Table 6). Log-transformed N₂O fluxes measured by the manual system were positively correlated ($p < 0.001$) to soil respiration rates ($r^2 = 0.58$), soil temperature in a depth of 3 and 10 cm ($r^2 = 0.64$) and air temperature ($r^2 = 0.58$). Correlation analysis between daily N₂O fluxes from the AGPS system and soil temperature revealed weaker but significant relationships ($r^2 = 0.27$, $p < 0.001$).

Nitrate and NH₄⁺ deposition via throughfall and NO₃⁻ concentration in the mineral soil showed significant positive effects on N₂O fluxes ($r^2 = 0.26$, $r^2 = 0.25$, $p < 0.001$ and $r^2 = 0.41$, $p < 0.05$), even higher correlation was found with NO₃⁻ concentration in the litter layer ($r^2 = 0.44$, $p < 0.01$).

Simple regression models were insufficient for revealing dependencies of emission data, as residuals were correlated over time. Two GARCH models could be developed to predict N₂O emissions as measured with the manually operated system. Independent variables in model 1 were (x_{1t}) soil moisture at a soil depth of 5 cm and (x_{2t}) soil temperature at

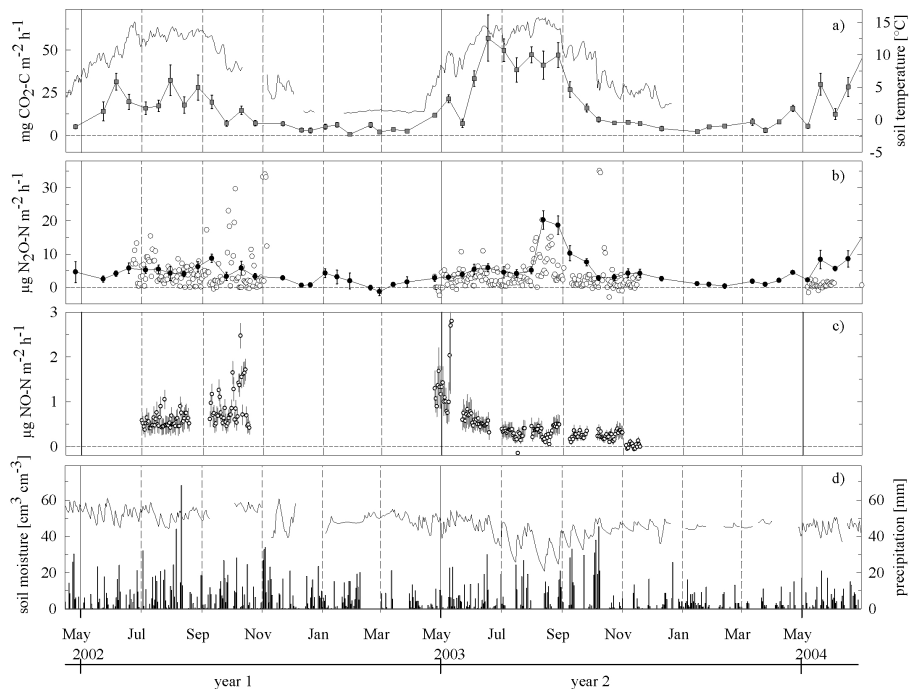


Fig. 3. (a) Mean CO₂ emissions (squares±S.E) measured with the manual chambers and soil temperature [5 cm] (line), (b) mean N₂O emissions from manual (dots±S.E) and automatic (circles) chambers, (c) mean NO emissions (±S.E) and, (d) daily precipitation (bars) and soil moisture [5 cm] (line) at the study site Achenkirch in the two investigation years.

Table 6. Matrix of Pearson correlation coefficients for significant relationships of mean N-emissions from manual chambers, AGPS system and dynamic chambers and soil-, meteorological- and N-input data at the site Achenkirch.

	lnN ₂ O-manual		lnN ₂ O-AGPS		lnNO
CO ₂	0.58	***			
Air temperature	0.58	***	0.16	*	
Soil temperature	0.64	*** a)	0.27	*** b)	0.19 ** b)
NO ₃ ⁻ -N litter layer	0.44	**			
NO ₃ ⁻ -N mineral soil	0.41	*			
TF NO ₃ ⁻ -N	0.26	***			
TF NH ₄ ⁺ -N	0.25	***			
TF sumN	0.31	***			
DRY_NH ₃ -N	0.37	**			

TF = throughfall, DRY = dry deposition. A moving average of 2 was applied to throughfall data. Soil temperature in ^{a)} 3 and 10 cm and ^{b)} in 5 cm. Asterisk indicates the statistic significance (* *p*<0.05, ** *p*<0.01, *** *p*<0.001).

a soil depth of 3 cm. As an effect of N-deposition on N₂O emission was discovered while carrying out the correlation analysis (Table 6), we included the monthly sum of nitrogen input (NO₃⁻ and NH₄⁺) via throughfall within model 2 and achieved an improvement of modelled N₂O emissions in comparison to simple regression analysis. Both models follow the GARCH (2, 1) process and revealed a *r*² of 0.89 (model 1) and *r*² of 0.83 (model 2) (Fig. 4). Daily N₂O emissions from the AGPS showed a high temporal variabil-

ity. Moreover, correlations with soil parameters were lower compared to the N₂O emissions measured by the spatially extended manual system. The GARCH model (Fig. 4, model 3 and Table 7) revealed that precipitation and air temperature on daily N₂O emissions are delayed by 8 days (*p*<0.001, *r*²=0.43).

Table 7. Parameter estimation for the autoregression models 1 to 4 to predict N₂O and NO emissions from the study site, Achenkirch. Parameters are based on data from the two investigation years. Intercept, regression coefficients of the independent variables (x_1) and (x_2) and significance level are shown for the individual models. a) in 5 cm, b) in 3 cm.

Model			1	2	3	4
independent variable (y_t):			N ₂ O-manual	N ₂ O-manual	N ₂ O-AGPS	NO
Intercept:	β_0		-12.9481	1.9971	7.0895	1.0429
regression coefficients of the independent variables (x_1) and (x_2) with significance level:						
β_1	(x_1)	soil moisture	0.2885			-0.0034
β_1	(x_1)	bulk N deposition		-0.4061		
β_1	(x_1)	precipitation			0.0851	
β_2	(x_2)	soil temperature	0.4753			-0.0308
β_2	(x_2)	air temperature			-0.1992	
total R²:			0.89	0.83	0.43	0.77
<i>n</i>			147	213	260	217

Regression coefficients and model parameters are statistically significant at the * $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$ level. Bulk N deposition = NO₃⁻-N and NH₄⁺-N in the throughfall.

3.3.3 NO_x fluxes

Mean NO emissions were $0.7 \pm 0.04 \mu\text{g N m}^{-2} \text{h}^{-1}$ and hence significantly larger in the first year ($p < 0.001$) compared to the second year ($0.5 \pm 0.07 \mu\text{g N m}^{-2} \text{h}^{-1}$) when low soil N concentrations were measured. Mean NO emissions were generally smaller than N₂O emission rates. A consistent seasonal trend could not be observed: In the first year largest emissions occurred in autumn, whereas in the second year maximum emissions were measured in spring (Fig. 3c). (NO_x-NO) was deposited with a mean of $-0.3 \pm 0.1 \mu\text{g N m}^{-2} \text{h}^{-1}$ (year 2).

Correlation analysis (Table 6) revealed a weak positive relationship between mean daily NO fluxes and soil temperature at the soil depth of 5 cm ($r^2 = 0.19$, $p < 0.5$). No valid statistical explanation could be given to characterize NO emissions by a simple regression model. By using the autoregression procedure, however, a GARCH (1,1) model could be developed to predict daily NO emissions of our site (Fig. 4, model 4). Through a mean of daily soil moisture content (x_{1t}) and soil temperature (x_{2t}) at a soil depth of 5 cm, predictions of mean daily NO emissions could be carried out with an r^2 of 0.77 (Table 7). This model revealed a time lag of 2, signifying that the independent variables have an influence on NO emissions over two days.

3.3.4 Acetylene inhibition

Acetylene inhibits the reduction of N₂O to N₂. The total N-emission due to denitrification can be measured. The production of N₂O in C₂H₂-treated samples was between 101 and 4200% (median: 266%) of the samples without inhibition. The ratio of N₂O-N:N₂-N was 1:6. Mean

N₂ production (\pm S.E) at a WFPS of 43% and 46% was $11.6 \pm 1.4 \mu\text{g N m}^{-2} \text{h}^{-1}$ and $19.1 \pm 3.9 \mu\text{g N m}^{-2} \text{h}^{-1}$.

4 Discussion

4.1 CO₂ fluxes

Carbon dioxide emissions, a measure for general microbial activity, followed a typical seasonal trend, with highest rates in summer, when mineralization of organic matter occurs. Lowest rates were measured in winter. Organic carbon is converted to CO₂ during mineralization. This process is strongly dependent on soil temperature and soil moisture. At our site, soil temperature at a soil depth of 3 and 10 cm was mostly responsible for temporal variation in soil respiration. This finding is in good agreement with results from other studies (Epron et al., 1999; Merino et al., 2004). Soil moisture also showed a significant effect on soil respiration rates. Carbon dioxide release was reduced during periods of heavy rain (summer 2002), when the water content was between 50–65%, probably as a consequence of O₂ deficiency in soil due to diffusion restrictions (Howard and Howard, 1993). The cumulative soil respiration rates at our site ($1\text{--}1.6 \text{ t CO}_2\text{-C ha}^{-1} \text{ y}^{-1}$) are lower than values for temperate coniferous forests reported by Raich and Schlesinger (1992).

4.2 N₂O fluxes

At our site, seasonal variations in N₂O emissions followed mainly the annual changes in soil temperature, soil moisture and the availability of N in the soil. Largest emissions were thus observed during summer/autumn. Although, we missed out on the summer peak in year 2002 through the manual

chamber system (biweekly sampling), we were able to observe large emissions by the AGPS.

Soil temperature and soil moisture were the most important factors controlling N₂O emissions. Those parameters affect microorganisms and their metabolism and, hence, the production and consumption of N trace gases in soils (Conrad, 1996). The air-filled porosity controls the movement of the gases towards and away from the atmosphere; it also affects soil aeration, and, thus, indirectly controls the capacity of the soil for producing or consuming soil-produced trace-gases (Smith et al., 2003; Davidson et al., 2000). In a laboratory parameterisation study, Schindlbacher et al. (2004) found for the AK site a N₂O emission maximum at a soil moisture range of 60%–90% water filled pore space (WFPS) which corresponds to a water content of 53–80%. In the field we found, beside the peak in August 2003, that maximum N₂O emissions occurred at soil moisture values in the range of 50%–65%, i.e. in accordance to the laboratory results of Schindlbacher et al. (2004). With the GARCH model 1 N₂O emissions could be predicted best using soil moisture and soil temperature as predictors ($r^2=0.89$). Within the model, soil moisture showed a highly significant effect ($p<0.001$); an effect of soil temperature was also visible ($p<0.01$). Furthermore, high precipitation and low air temperature showed a significant effect on N₂O emissions with a lag of ~8 days (model 3). We hypothesize that these adverse conditions for microbes may be comparable to the effects observed after freeze-thaw events. In a microcosm experiment Sharma et al. (2006) found that maximum N₂O emissions occurred ~8 days after thawing.

Largest emissions were observed in the second year in August. There are various parameters that might have contributed to the N₂O peak. Even at this site, where soil moisture is generally high, the water content during the European drought period of summer 2003 decreased to 30%. After a rainfall event soil moisture increased again and may have caused an increase in microbial activity. On the other hand, the actual level of N-deposition and the NO₃⁻ pool in the soil might have played an important role in the sudden release of N₂O (Davidson et al., 2000). Highest amounts in NO₃⁻ and NH₄⁺ via throughfall reached the forest floor in August. Although, throughout the study bulk N-deposition accounted for up to only 31% of the variation in N₂O emission (correlation analysis), a strong relationship was apparent between the two factors. This high N₂O peak coincided with significant larger available soil N concentrations, in particular soil NO₃⁻. Using model 2 the relationship between biweekly measured N₂O emissions and biweekly sum of nitrogen input (NO₃⁻ and NH₄⁺) via throughfall was found by a high r^2 (0.83). The time series analysis revealed a highly significant ($p<0.001$) lagged effect of reduced bulk N-deposition on N₂O emission for a 3-month period. Model 1 also revealed that past environmental conditions (3 months) of high soil moisture and temperature can significantly affect actual

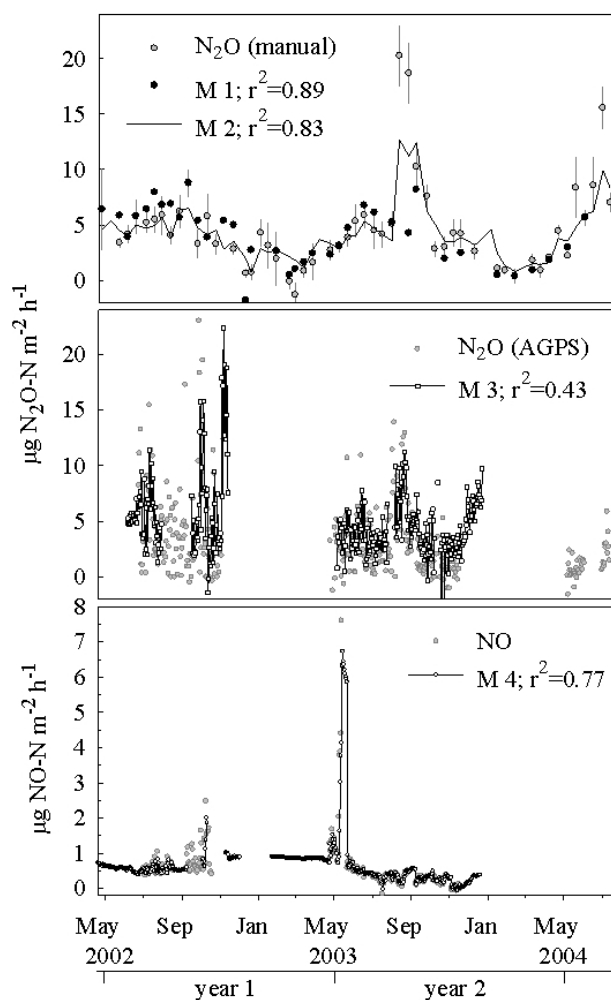


Fig. 4. Predicted versus measured N₂O and NO emissions at Achenkirch in the two investigation years. Independent variables are soil moisture and soil temperature for model 1 (M 1) and model 4 (M 4); N-deposition (NH₄⁺-N and NO₃⁻-N) for model 2 (M 2) and, precipitation and air temperature for model 3 (M 3).

N₂O emissions. Explanations for this phenomenon can only be hypothetical. It has been observed that nitrogen in microbes may have a turnover rate of ~3 months (Tietema and van Dam, 1996). According to the theories of microbial stoichiometry (Schimel and Weintraub, 2003) microbes tend to immobilize nitrogen from the soil solution and use it for cell growth at times when it is the limiting nutrient. This could be the case during favourable growth conditions of soil moisture and high temperatures but little N-input. After ~3 months microbial death may occur, which may lead to enhanced N-release and N₂O emissions as observed in beech forests (Zechmeister-Boltenstern et al., 2002).

The soil at the Mühleggerköpf is typically moist (mean 55%) and denitrification may have been the main source of N₂O emissions throughout the year. A high pH value is also one of the factors that provide favourable conditions

for denitrification at the site. Previous studies (Härtel et al., 2002) have indicated that complete nitrification takes place at our site and that it is of major importance for N₂O emission. ¹⁵NO₃⁻ was strongly immobilized. Furthermore, close C/N-ratios (16–18) suggest favourable conditions for N-mineralization and nitrification (Herman et al., 2002). It was in August/September that nitrate concentration increased and we suppose that the high N₂O peak in the second year is the product of nitrification.

At our site winter emissions were generally small and the site even functioned as a sink for N₂O. Butterbach-Bahl et al. (2002) detected negative N₂O fluxes in pine forests with moderate N-deposition whereas a pine forest with high N-loads exclusively functioned as a source of N₂O during winter. On the other hand winter emissions, comparable to the ones during the year (January 2003; $4.3 \pm 1.3 \mu\text{g N}_2\text{O-N m}^{-2} \text{h}^{-1}$), could be observed after freeze-thaw events. These large emissions were either a result of enhanced denitrification activity or could be due to the physical release of accumulated N₂O in the snow or in the soil (Teepe et al., 2001).

4.3 NO_x fluxes

The production of NO is strongly dependent on climate and varies considerable with soil temperature and soil moisture (Davidson et al., 2000; Ludwig et al., 2001; Van Dijk et al., 2002). The optimum soil temperature (20°C), as detected in laboratory studies by Schindlbacher et al. (2004), could not be confirmed in the field experiment, where largest NO emissions were measured at 8–10°C soil temperature; maximum soil temperature in the field was 16°C. Optimum WFPS in the field for NO emission was found to be at 30–45% WFPS (water content 27–40%) and was, thus, higher than in laboratory studies (Schindlbacher et al., 2004). In the field largest NO emissions were found in autumn and in spring, when soil water content was between 45–50%. Large spring emissions were detected in May, when soil was moistened and soil temperature increased. With the GARCH procedure a relationship between NO emissions and soil moisture and soil temperature could be found with an $r^2=0.77$ (model 4). Autoregressive parameters were estimated for a time-lag of 2 days; i.e. NO emissions were especially promoted when soils had been colder and drier ~2 days before.

Soil nitrogen content contributed to large NO emission in autumn, where highest NO₃⁻ and NH₄⁺ concentrations were measured. As in autumn 2003 the N-pool (especially extractable NH₄⁺) in the soil and the litter layer was low compared to concentrations measured in autumn 2002 no increase in NO emissions could be detected. The effect of rewetting the soil as it was found for N₂O emissions could not be seen for NO emissions.

Soil acidity is supposed to be an important factor promoting N-emissions from forest soils influenced by atmospheric nitrogen deposition (Li et al., 2000 and Venterea et

al., 2003). Soils with a pH of 7–8 are supposed to produce higher amounts of N₂ (Simek and Cooper, 2002) but revealed an order of magnitude larger N₂O emissions than soils with a pH between 4 and 6 (Vermoesen et al., 1996). A soil pH of 6.7–7.1 measured at our limestone site restricts self-decomposition of HNO₂ and might, therefore, be responsible for small NO fluxes (Van Cleemput and Samater, 1996). Beside the high pH and the high microbial biomass (Härtel et al., 2002), the well-balanced community composition of the microflora could be a reason for small NO-fluxes. Results of PLFA (Phospholipid fatty-acid analysis) studies of European soils by (Zechmeister-Boltenstern, unpublished) showed that at acidic high N-input sites the microbes are under stress which leads to structural changes of their cell membranes. This could cause losses of intermediate products in the nitrification or denitrification pathway and could, thereby, lead to larger NO and N₂O emissions. The assumption of a well-balanced microflora was supported by the acetylene inhibition experiment.

4.4 Annual N-emissions

At our site the N release was between 0.3 and 0.4 kg N₂O-N ha⁻¹ y⁻¹, and 0.03 kg NO-N ha⁻¹ y⁻¹ (Table 5). These values correspond to a yearly release of actual N input of 2.5–3.5% in form of N₂O-N and 0.2% in form of NO-N and are located in the lower reported percentage of deposited N which is 0–16% (N₂O-N) and 0–10% (NO-N) (Skiba et al., 2004). According to the acetylene inhibition method the ratio of N₂:N₂O was 6.0. The estimated annual N₂ emission is therefore 2.2 kg N ha⁻¹. The ratio of N₂:N₂O is considerably higher than in previous investigations of forests (0–0.4; Wolf and Brumme, 2003; Brumme et al., 1999; Mogge et al., 1998). Our estimation is based on only two measurements. Conclusions need to drawn cautiously because the N₂ production changes with changing WFPS% (Davidson et al., 2000). However, it can be hypothesized that the deposited N from the atmosphere is mainly emitted as N₂ at this limestone site.

The magnitude of N₂O-N emissions from our site is consistent with values reported of other coniferous forests (MacDonald et al., 1997; Papen and Butterbach-Bahl, 1999; Butterbach-Bahl et al., 2002) and limed beech forests (Borken and Brumme, 1997). Higher emissions (16–35 N₂O-N m⁻² h⁻¹) have been measured from acidic soils of N-enriched coniferous forests (Papen and Butterbach-Bahl, 1999; Butterbach-Bahl et al., 2002) and from deciduous forests (1.5–5.6 kg N₂O-N ha⁻¹ y⁻¹) with low pH (Brumme and Beese, 1992; Borken and Brumme, 1997).

Nitric oxide emission measured in our study are small in comparison to other published NO fluxes from temperate coniferous forests. Our rates are in accordance with studies by Johansson, (1984) who reported annual NO emissions of 0.04 kg NO-N ha⁻¹ y⁻¹ from an unfertilized coniferous forest soil in Sweden. The majority of studies, however,

revealed significantly larger values. Pilegaard et al. (1999) and Butterbach-Bahl et al. (2002) found in moderately N-effected spruce forests annual NO emissions of 3.15 kg NO-N ha⁻¹ y⁻¹ and 3.1 µg NO-N m⁻² h⁻¹, respectively. It has to be taken into account that most of the reported data were measured at forest soils with low pH values; however, NO fluxes are reported to be significantly larger in more acidic soils compared to N₂O fluxes (Yamulki et al., 1997).

The employed GARCH model predicts NO fluxes with a higher r^2 than a regression model. Nitrous oxide emissions measured by manual chambers yielded an r^2 of 0.89 (model 1) and an r^2 of 0.83 (model 2). Through model 2, with N-deposition as the only independent variable, annual emission rates were better than with model 1, where soil moisture and soil temperature were the independent variables. Especially in the second year, where large emissions (singular event) were detected in August, the predicted emissions with model 2 had a higher R-squared as with model 1. High variations in N₂O emissions measured by the AGPS led to an overestimation of N₂O emissions through model 3 (21–27%). Daily measured NO emissions were predicted with an r^2 of 0.77 (model 4) and also the high peak in May was captured. Annual simulated fluxes were in accordance with measured annual NO emissions.

We conclude that the GARCH model is better than a conventional regression analysis, because soil N-emissions can be modelled with a higher r^2 . It reflects lagged effects of soil moisture, soil temperature, precipitation, air temperature and N-deposition on N-oxide emissions. The use of time-series models in GHG-flux investigations is a novel approach in soil science. So is the search for time-lagged responses of gas fluxes to environmental factors. At our site, NO emissions were three times smaller compared to N₂O emissions and total emissions of N were small compared to N-inputs. This may be attributed to the fact that in the limestone Alps soil pH is high, a large microbial biomass can be found and nitrogen is mainly emitted in the form of N₂. Alone in Austria, about a third of forests are on calcareous bedrock and this is the first report on processes determining N-oxides fluxes in these ecosystems.

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